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PHOTOCHEMICAL DECOMPOSITION OF SILK[1]

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ABSTRACT

The purpose of this investigation was to study the deterioration of silk on exposure to daylight under natural conditions of use.

The strength of silk cloth decreased and its ammonia nitrogen content increased on exposure to sunlight. Samples of the cloth treated with a tenth normal solution of sodium hydroxide showed smaller changes and samples treated with a tenth normal solution of sulphuric acid greater changes than the untreated cloth under the same conditions.

Similar results were obtained on exposure of samples to north skylight. Samples treated with sodium carbonate solution of 1 percent or less in concentration showed the greatest stability.

The amino nitrogen content was the same for silk stored in the dark and silk exposed to sunlight for 3 months. The rate of hydrolysis in 0.5 normal sodium hydroxide solution, measured by the formation of amino nitrogen, was the same for both samples.

The decrease in breaking strength and increase in ammonia nitrogen content of silk on exposure to light are brought about by atmospheric oxidation in the presence of light.

The results of these experiments are in accord with those obtained in the accelerated aging tests of silk, using the carbon arc lamp as a light source.

CONTENTS

I. INTRODUCTION

Previous work [3] has shown that when silk is exposed to the radiation of a glass-enclosed carbon arc lamp, the extent to which it is weakened depends upon its "pH" (as defined by the pH of an aqueous extract). Silk was found to have maximum stability at about pH 10. As the pH was increased above pH 11 and decreased below pH 3, the stability of the silk decreased rapidly. Silk treated with 0.1 normal sodium-hydroxide solution was more stable to the action of light than untreated silk or silk treated with 0.1 normal sulphuric acid and the latter was the least stable.

[1] The work reported here was made possible by a grant from the Textile Foundation, Inc., to the American Association of Textile Chemists and Colorists.

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[3] M. Harris and D. A. Jessup. The Effect of pH on the Photochemical Decomposition of Silk. B.S. Jour. Research, vol. 17, p. 1179–1184, 1931.

The purpose of the present investigation was to study the deterioration of silk on exposure to daylight under natural conditions of use. Both the chemical and the physical breakdowns were followed. The experiments were designed to show something of the nature of the photochemical reaction.

II. EXPERIMENTAL

The general procedure was that used in the previous work and has been described.[4] The decrease in breaking strength of the cloth with duration of exposure was taken as a measure of the physical breakdown of the silk. The chemical breakdown was followed by analyzing specimens for ammonia nitrogen and amino nitrogen. The former is that portion of the nitrogen which is liberated when the silk is boiled in a saturated solution of magnesium oxide. The latter is the portion obtained when the silk is treated with nitrous acid, using the method of Van Slyke.[5]

One series of experiments was concerned with the effect of sunlight. Degummed silk was purified by successive extractions with alcohol and ether and then washed for one-half hour with water at 60 C to remove any adsorbed solvent. Some samples of the silk were soaked in 0.1 normal sodium-hydroxide solution and others in 0.1 normal sulphuric-acid solution for 10 minutes. The excess liquor was removed by centrifuging and the samples were air-dried. Samples of purified acid-treated and alkali-treated silk were then exposed to sunlight. The exposures were continuous day and night, regardless of the weather, under glass at an angle of 45°, facing south. At the end of 15 days the alkali-treated silk had a breaking strength of 53 pounds, the untreated sample 38 pounds, and the acid-treated sample 8 pounds. The strength of the original cloth was 55 pounds. At the end of 4 months the untreated and acid-treated silk had practically no strength but the alkali-treated silk still had 10 percent of its original strength.

At intervals of time samples were analyzed for ammonia nitrogen. The results are given in table 1. All of the exposed samples gave increasing amounts of ammonia nitrogen with increasing duration of exposure, the greatest amounts being present in the acid treated and untreated samples.

TABLE 1.—*Effect of sunlight exposure on ammonia nitrogen content of silk.*

[The number of milligrams of ammonia nitrogen per gram of silk is given]

Time of exposure, days	Untreated silk		Silk treated with	
	Not exposed	Exposed	0.1 N NaOH	0.1 N H_2SO_4
32	0.10	0.31	0.16	0.87
69	.08	.37	.22	1.03
90	.10	.64	.45	2.05
104	.09	.75	.52	2.09
130	.07	1.06	.64	2.81
150	.12	2.00	.95	2.92
175	.11	2.60	1.03	2.99

[4] See reference footnote 3.

[5] D. D. Van Slyke, The Quantitative Determination of Aliphatic Amino Groups, Jour. Biol. Chem., vol. 12, p. 275–84, 1912.

The total nitrogen content, amino-nitrogen content, and rates of hydrolysis of the purified silk (not treated with acid or alkali) which had not been exposed to strong light and which had been exposed to sunlight for 3 months were determined. The sample for analysis was ground to a fine powder. In order to determine rate of hydrolysis, about 5 grams of the powder was shaken in 200 ml of water for 4 hours, using an automatic shaker. The larger particles of silk were allowed to settle and the supernatant liquor was decanted and mixed with an equal volume of 1 normal sodium hydroxide solution. The mixture was kept in a bath at 37 C. Ten ml aliquots were withdrawn at definite intervals of time and analyzed for amino nitrogen and for total nitrogen. The results are shown in figure 1. Neither the unexposed nor the exposed silk contained an appreciable amount of amino nitrogen before hydrolysis. The rate of hydrolysis, measured by the formation of amino nitrogen, was the same for both samples.

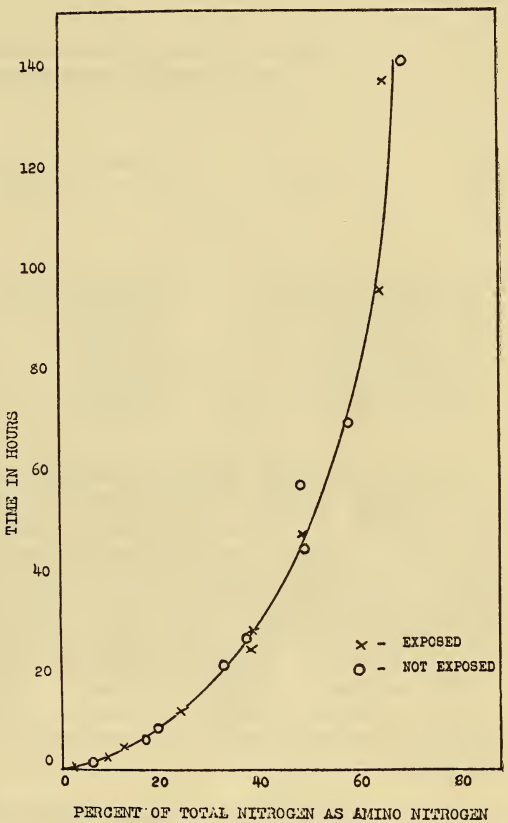

FIGURE 1.—*The rates of hydrolysis of silk which had not been exposed to strong light and which had been exposed to sunlight for 3 months.*

Another series of experiments was concerned with the deterioration of silk cloth treated with acid and alkaline solutions on exposure to north skylight. The samples were exposed continuously in a room behind window glass, vertical, facing north. Plain-weave cloth weighing approximately 1.6 ounces per square yard was cut into pieces about 1 yard square. These were purified by scouring in a 0.5 percent soap solution at 60 C for 20 minutes; rinsing in 3 successive baths of water at 60 C for 20 minutes each; extracting with alcohol and ether for 24 hours each; and finally washing with water at 60 C for 30 minutes. The individual cloths were soaked for 5 minutes in the solutions listed below, centrifuged, and dried at 70 F and at a relative humidity of 65 percent.[6]

(1) No treatment; (2) 0.01 *N* sulphuric acid; (3) 0.01 *N* acetic acid; (4) 0.1 percent sodium carbonate; (5) 0.5 percent sodium carbonate;

[6] The amount of reagent remaining on the fiber may be roughly estimated by assuming that after centrifuging, the silk retains its own weight of solution.

(6) 1.0 percent sodium carbonate; (7) 1.5 percent sodium carbonate; and (8) 0.75 percent sodium bicarbonate.

The breaking strength and appearance of each cloth after exposure for stated periods of time are given in table 2. The acid-treated samples showed the greatest deterioration, the untreated sample was much more stable, and the samples treated with sodium carbonate solutions in concentrations of 1 percent or less showed the greatest stability. These results are in accord with those obtained in the accelerated aging tests of silk, using the carbon-arc lamp as a light source.

TABLE 2.—*The appearance and breaking strength of silk treated with acid or alkaline solutions after exposure to north light*

Sample no.	Treatment	Appearance after exposure for 11 months	Breaking strength (1-inch strip) after—		
			5½ months	7½ months	11 months
			Pounds	*Pounds*	*Pounds*
1	Original (not exposed)	No change	37	37	36
2	0.1 percent Na_2CO_3	Very slightly yellow	34	30	30
3	1.0 percent Na_2CO_3	Slightly yellow	32	29	27
4	0.5 percent Na_2CO_3	Faint yellow	32	29	26
5	None (exposed)	No change	30	29	24
6	1.5 percent Na_2CO_3	Yellow	30	27	23
7	0.75 percent $NaHCO_3$	Faint yellow	28	24	20
8	0.01 N acetic acid	No change	17	16	14
9	0.01 N sulphuric acid	Faint yellow	14	13	12

After 11 months' exposure, samples of the cloth were analyzed for ammonia nitrogen and amino nitrogen. Portions of each cloth were dried for 6 hours at 105 C and the ammonia nitrogen determined. The silk was then thoroughly washed and again dried for 6 hours at 105 C. One-gram portions were dissolved in 20 ml of a 50 percent lithium bromide solution at 80 C and the solution diluted to 100 ml in a volumetric flask. The amino-nitrogen content of each solution was determined. The results of the analyses are given in table 3.

The decrease in breaking strength is accompanied by an increase in the ammonia nitrogen content of the silk. The amino-nitrogen content does not appear to be affected during the deterioriation of the fiber.

TABLE 3.—*The ammonia- and amino-nitrogen content of silk treated with acid or alkaline solutions after exposure to north light for 11 months*

Sample no.	Treatment	Ammonia nitrogen	Amino nitrogen
		Mg/g silk	*Mg/g silk*
1	None (not exposed)	0.07	1.5
2	0.1 percent Na_2CO_3	.15	1.6
3	1.0 percent Na_2CO_3	.15	1.4
4	0.50 percent Na_2CO_3	.23	1.4
5	None (exposed)	.44	1.4
6	1.5 percent Na_2CO_3	.19	1.4
7	0.75 percent $NaHCO_3$	.39	1.7
8	0.01 N acetic acid	.72	1.5
9	0.01 N sulphuric acid	1.08	1.4

III. NATURE OF THE PHOTOCHEMICAL REACTION

The photochemical decomposition of silk is a photo-oxidation reaction. Skeins of 20/22 Japanese silk have been exposed in vacuum and in atmospheres of moist and dry hydrogen and oxygen to north sky light for 4 months. The skeins in the vacuum and in the hydrogen retained their original strength. Those in the dry oxygen lost about 3 percent while those in moist oxygen lost about 10 percent of their strength.

The increase in ammonia nitrogen content of silk during the photochemical deterioration is further evidence that an oxidation reaction has taken place. Palit and Dhar [7] have shown that in the decomposition of most nitrogenous substances, ammonia is formed and the decomposition is accelerated by the presence of oxygen and light. The deterioriation of wool in the carbonizing process is also accompanied by the formation of ammonia, the amounts formed increasing with increasing acid and moisture contents of the wool and with increasing temperatures in the baking oven. When wool containing sulphuric acid is stored at ordinary temperatures, the ammonia-nitrogen content increases with increasing time of storage. When acid treated and untreated specimens of wool were baked in atmospheres of dry on moist air, oxygen, or carbon dioxide showed that both oxygen and moisture have an important influence on the deterioriation of wool. Sulphuric acid increases the rate of deterioration considerably.[8] Leiben and Urban [9] found that the splitting of ammonia from amino acids and other substances proceeds much more rapidly in acid than in alkaline or neutral solutions. Schanz [10] studied the action of ultraviolet rays on egg and serum proteins He found that the greatest change was produced in acid solution and that the reaction was accelerated by oxygen.

The experimental results of this research are in accord with those obtained by other workers in studying the action of light on protein materials. The decrease in breaking strength and increase in ammonia-nitrogen content of silk during exposure are caused by the action of the oxygen of the air in the presence of light.

Washington, May 4, 1934.

[7] Palit and Dhar. Oxidation of Carbohydrates, Fats, and Nitrogenous Products by Air in the Presence of Sunlight. Jour. Phys. Chem., vol. 32, p. 1263, 1928.
[8] M. Harris. The Carbonization Process: A Study of the System Wool-Sulphuric Acid-Water. B.S. Jour. Research, vol. 12, pp. 175–87, 1931.
[9] F. Lieben and F. Urban. The Splitting of Ammonia From Amino Acids and Other Substances in the Light of a Quartz Lamp. Biochem. Zs., vol. 239, pp. 250–56, 1931.
[10] Schanz. Arch. ges. Physiol., vol. 164, p. 445, 1916.